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COMPETING UNIMOLECULAR REACTIONS OF FLAME RADICALS.   I. ISOMERIZATION AND DISSOCIATION OF THE METHOXY RADICAL

George F. Adams

November 1985

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Ab initio electronic structure calculations provide chemical energy
differences necessary for statistical mechanical rate coefficient estimates.
We report the results of many-body perturbation theory results for two
unimolecular reactions of the methoxy radical. Rate coefficient estimates
for the dissociation (H-atom scission), and isomerization (1,2-hydrogen
shift) reactions infer that these reactions compete at high temperatures.

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I. INTRODUCTION

Flame chemistry models for even simple chemical oxidations include hundreds of chemical reactions. Commonly, rate coefficient data is available for few of the proposed reactions. In some cases, reaction network schemes do not provide even qualitative descriptions of the observed chemistry. The methoxy radical, CH_3O, appears as a constituent in chemical models that describe the oxidation of fuels, especially combustion systems. Numerous experimental[1-10] and theoretical[11-19] research projects have focused upon this

1. K. Iwasaki and K. Tariyama, "Electron Spin Resonance of Methoxy Radicals Trapped in the Methanal Irradiated at 4.2K," *J. Am. Chem. Soc.*, Vol. 100, p. 1964, 1978.

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16. C.F. Jaeckels, "Electronic Structure Calculations for Methoxy: The X^2E and A^2A_1 States," J. Chem. Phys., Vol. 76, p. 505, 1982.

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19. S. Saebo, L. Radom, and H.F. Schaefer, III, "On the Weakly Exothermic Rearrangement of Methoxy Radical (CH_3OH)," J. Chem. Phys., Vol. 78, p. 845, 1983.

radical. Most of these researches attempted to elucidate the molecular structure and spectroscopy of this radical; tasks which remain incomplete, however. To date, no empirically derived structure has been obtained, nor has the complete vibrational spectrum been determined. While such characterization studies continue, the chemical reactions that include the radical populate nearly all combustion models. Here too, the lack of experimental and theoretical information leads to great uncertainty in estimating rate coefficients for these reactions. Our previous research on this radical[17] was motivated, in part, by uncertainty in rate coefficient data for the hydrogen dissociation reaction,

$$CH_3O \rightarrow CH_2O + H \qquad\qquad (1)$$

Since methoxy is but one hydrogen atom more complex than formaldehyde, we also considered the 1,2-hydrogen shift reaction that isomerizes methoxy to form hydroxymethyl

$$CH_3O \rightarrow CH_2OH \qquad\qquad (2)$$

As was the case with the formaldehyde results,[20] the electronic energy barrier for methoxy isomerization was only slightly higher than the dissociation barrier. This result supported Radford's interpretation of experimental data suggesting that the isomerization reaction (Eq. 2) may compete with the dissociation reaction (Eq. 1).[21] Subsequently, Batt, Burrows, and Robinson[22] estimated an activation energy for the isomerization reaction, and concluded that the dissociation reaction dominates at high temperature. They noted, however, that the rearrangement reaction may compete with the dissociation at high temperature.

This report describes electronic structure calculations pertinent to these two reactions of methoxy. The quantum chemical results are used to obtain rate coefficient estimates for these two reactions for both low and high temperatures, in the low pressure limit region.

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20.   J.D. Goddard and H.F. Schaefer, III, "The Photodissociation of Formaldehyde: Potential Energy Surface Features," J. Chem. Phys., Vol. 70, p. 5117, 1979.

21.   H.F. Radford, "The Fast Reaction of CH$_2$OH with O$_2$," Chem. Phys. Letters, Vol. 71, p. 195, 1980.

22.   L. Batt, J.P. Burrows, and G.N. Robinson, "On the Isomerization of the Methoxy Radical: Relevance to Atmospheric Chemistry and Combustion," Chem. Phys. Letters, Vol. 78, p. 467, 1981.

II. THEORETICAL CHEMISTRY OVERVIEW

The description of chemical reaction pathways using quantum chemical methods has been simplified by the introduction of analytic formulas for the gradient of the energy and the second-derivatives of the energy.[23] This research employed the use of analytical energy gradients, computed with reference to unrestricted Hartree-Fock (UHF) wavefunctions, to locate those points on the energy hypersurface where the gradients vanish. Such points correspond to equilibrium structures, when there are no negative second-derivatives, and transition state structures, when there is one and only one negative second derivative. Structural parameters and second-derivatives for the methoxy radical, and the two transition states were obtained using the GRADSCF system of electronic structure codes.[24] These UHF calculations obtained wavefunctions expanded in a 6-31G** basis set.[25] Subsequent structural optimizations obtained using a Dunning-Huzinaga double-zeta basis set[26] augmented by polarization functions on all atoms[27] did not yield significantly different results.

Self-consistent field methods, like UHF, yield unreliable predictions of chemical energy differences. These methods exclude the effects of correlated electron motions. There are a number of quantum chemical methods available to estimate the correlation-energy contribution. In this study, we have used the linked-cluster based method known as many-body perturbation theory (MBPT). The reference function for the MBPT calculations was taken to be a UHF wavefunction in the double-zeta plus polarization basis set. The MBPT calculations are fourth-order calculations that include all single-, double-, and quadruple-excitation diagrams that contribute at fourth-order.

23. M.J. Page, P.W. Saxe, B.H. Lengsfield, III, and G.F. Adams, "On the Development of MCSCF and MCSCF-CI Methods for the Calculation of Hessian Matrices," to be published.

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25. P.C. Hariharan and J.A. Pople, "Accuracy of AH_m Equilibrium Geometries by Single Determinant MO Theory," Mol. Phys., Vol. 27, p. 209, 1974.

26. T.H. Dunning, Jr., "Gaussian Basis Functions for Use in Molecular Calculations. I. Contraction of (9S5p) Atomic Basis Sets for First-Row Atoms," J. Chem. Phys., Vol. 53, p. 2823, 1970.

27. T.H. Dunning and P.J. Hay, "Gaussian Basis Sets for Molecular Calculations in Modern Theoretical Chemistry, Methods of Electronic Structure Theory," Vol. 3, H.F. Schaeffer, editor, 1977.

To estimate the unimolecular rate coefficients we use a simplified theory of unimolecular reactions developed by Troe.[28,29] Troe's review paper[29] cites the lack of detailed knowledge of the potential energy hypersurfaces and the intermolecular energy transfer processes as deficiencies that hamper the development of predictive rate coefficient models. The electronic structure calculations reported here, and in references 15 and 17, provide useful information about the potential energy hypersurfaces for the methoxy radical. Details of the energy transfer processes stand beyond the scope of this work. Troe's model avoids the energy transfer processes by invoking the strong collision hypothesis, and seeking ways to correct this overestimate.

Troe[29] expresses the limiting low-pressure pseudo-first-order rate coefficient, k_0, as

$$k_0 = \beta_c \, k_0^{sc} , \tag{3}$$

where β_c represents the temperature dependent collision efficiency and k_0^{sc} represents the strong-collision form of the limiting rate coefficient. The strong-collision rate coefficient is expressed as

$$k_0^{sc} = [M] \, Z_{LJ} \, \frac{\rho(E_o)kT}{Q_v} \, F_E F_{rot} F_{anh} \, \exp \, (-E_o/kT) , \tag{4}$$

where Z_{LJ} is the Lennard-Jones collision frequency, $\rho(E_o)$ is the harmonic density of states, Q_v is the vibrational partition function, and the F terms are correction factors for the energy dependence of the density of states, rotational effects and anharmonicity, respectively. The exponential contains the critical energy, E_o, the energy difference between the reactant and the transition state measured between the vibrational zero-points. In this work, we used expressions given by Troe in Reference 27 to evaluate the factors of k_0^{sc}.

A more precise approach to the treatment of competing reactions requires that we treat the two reactions simultaneously. Formally, for a two-channel competing reaction process, the total and single-channel rate coefficients are given by[30]

28. J. Troe, "Theory of Thermal Unimolecular Reactions at Low Pressures. II. Strong Collision Rate Constants Applications," J. Phys. Chem., Vol. 66, p. 4758, 1977.

29. J. Troe, "Predictive Possibilities in Unimolecular Rate Theory," J. Phys. Chem., Vol. 83, p. 114, 1979.

30. Th. Just and J. Troe, "Theory of Two-Channel Thermal Unimolecular Reactions. I. General Formulation," J. Phys. Chem., Vol. 87, p. 3068, 1980.

$$k_0 = {}_{E_{01}}\!\!\int^{\infty} h(E) \; f(E) \; [k_1(E) + k_2(E)] \; dE \tag{5}$$

$$k_{10} = k_0 - k_{20} \tag{6}$$

$$k_{20} = {}_{E_{02}}\!\!\int^{\infty} h(E) \; f(E) \; k_2(E) \; dE \tag{7}$$

where k_{10} represents the rate coefficient for the channel with the lower
critical energy and k_{20} that for the channel with the higher critical energy,
$h(E)$ is the population of reactive states above the lower threshold energy,
and $f(E)$ is the equilibrium population at energy E. Specific expressions for
the total rate-coefficient are

$$k_0 = [M] \; Z \; \frac{\rho(E_{01})kT}{Q_v} \; \exp \; (-E_{01}/kT) \; F_E \; (\frac{\alpha}{\alpha + F_e kT})^2 \tag{8}$$

where E_{01} is the critical energy for the lower critical energy channel,
and α represents the average energy removed in down transitions. The
corresponding expression for the upper-channel rate coefficient is

$$k_{02} = k_0 \; \exp \; (- \frac{(E_{02}-E_{01})(\alpha + F_E kT)}{\alpha F_E kT})*$$

$$[(\frac{\alpha + F_E kT}{\alpha F_E kT}) \; {}_{E_{02}}\!\!\int^{\infty} (\frac{k_2(E)}{k_1(E)+k_2(E)})*$$

$$\exp \; (- \frac{(E-E_{02})(\alpha + F_E kT)}{\alpha F_E kT})dE] \tag{9}$$

The integral appearing in the last equation can be approximated in various
ways. If the specific branching ratio

$$V_2(E) = \frac{k_2(E)}{k_1(E)+k_2(E)} \; , \tag{10}$$

varies only slightly with energy, then the ratio will be nearly equal to
$V_2(E_{02})$. If $V_2(E)$ varies markedly with E, then the specific rate constants
$k_1(E)$ and $k_2(E)$ must be used in evaluating the integral, or an exponential
model must be used to approximate $V_2(E)$. Since we're interested in the
variation of the rate coefficients with temperature over a large temperature
range, the evaluation of the specific branching ratio will be treated in a
consistent manner. A more thorough discussion of the theory of two-channel
unimolecular reactions is given by Just and Troe.[30] The treatment used in

this study assumes a vibrational two-channel model for the low-pressure limit of the unimolecular reaction. Both unimolecular reactions of the methoxy radical are characterized by rigid transition state complexes.

III. ELECTRONIC STRUCTURE THEORY RESULTS

In our previous report on the unimolecular reactions of the methoxy radical,[17] we reported structural parameters for CH_3O and a series of transition states relevant to the chemistry of the radical. As noted by Saebo, et al,[19] the structure reported in Reference 17 for the methoxy radical corresponds to the $^2A''$ component of the ^2E state, rather than the $^2A'$ ground state. The correct structural parameters and electronic energy are reported for the X^2A' state of methoxy in this report. The transition state structures cited in Reference 17 correspond to points on the $^2A'$ hypersurface. Thus, the electronic contribution to the critical energies equals the electronic energy differences between the two transition state structures and the equilibrium structure. Table 1 contains a summary of the structural information for the radical and the transition states, and Table 2 contains the results of the electronic energy calculations obtained with the double zeta plus polarization basis set at several levels of theory. The most accurate energy differences should be those predicted by fourth-order MBPT; thus, the electronic energy barriers equal 35.2 kcal/mole and 35.6 kcal/mole for dissociation and isomerization, respectively.

TABLE 1. OPTIMIZED GEOMETRICAL PARAMETERS FOR STATIONARY POINTS
ON THE METHOXY SURFACE[a],[b]

CH_3O (X^2A')
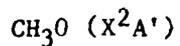
$r(C-H_1)$	1.086
$r(C-H_3)$	1.089
$r(C-O)$	1.382
OCH_1	111.7
OCH_3	106.1
H_1CH_2	110.5

Transition Structure: Dissociation

$r(C-H_1)$	1.087
$r(C-H_3)$	1.834
$r(C-O)$	1.225
OCH_1	121.4
OCH_3	99.8
H_1CH_2	116.7

Transition Structure: Isomerization

$r(C-H_1)$	1.078
$r(C-H_3)$	1.264
$r(C-O)$	1.367
OCH_1	117.4
OCH_3	53.5
H_1CH_2	118.3

a – Units: Bond Lengths, Angstroms.
b – Units: Bond Angles, Degrees.

TABLE 2. ELECTRONIC ENERGIES (UNITS: HARTREES)

	Radical Equilibrium	Transition State Dissociation	Transition State Isomerization
UHF	-114.4484	-114.3845	-114.3668
SDQ-MBPT(4)	-114.7621	-114.7060	-114.7054

To determine the critical energy for reaction requires knowledge of the zero-point vibrational energy for the reactant and transition state. By computing the second-derivatives of the molecular energy with respect to nuclear distortion, we can determine the harmonic vibrational frequencies for these structures. The harmonic frequencies for the methoxy radical and the two transition states are presented in Table 3. Note that each of the transition states has one, and only one, imaginary frequency. With these results, we estimate the critical energy for dissociation to be 29.5 kcal/mole, while that for isomerization is 31.7 kcal/mole.

TABLE 3. VIBRATIONAL FREQUENCIES FOR POINTS ON THE METHOXY HYPERSURFACE
(UNITS: WAVENUMBERS)

Equilibrium	Dissociation TS*	Isomerization TS*
3274	3768	3366
3255	3138	3249
3188	1708	2473
1668	1518	1621
1604	1345	1266
1585	1211	1241
1283	668	1074
1226	504	945
1130	955i	2569i

*Transition State.

To anticipate our treatment of the rate coefficients, we note that the vibrational frequencies for the methoxy radical share the defect of all frequencies determined using SCF analytical gradients. Such frequencies are estimates of harmonic vibrations, while empirically observed vibrational frequencies include anharmonic character. The experience of quantum chemists in computing frequencies suggests that the results reported in Table 3 will exceed observed frequencies by approximately 10%. Therefore, we reduce the predicted frequencies before use in the rate coefficient estimation.

IV. RATE COEFFICIENT ESTIMATES

The rate coefficients for dissociation and isomerization of the methoxy radical for temperatures in the range, 300K < T < 1200K, are evaluated in two ways. We present first the results of separate calculations of the two processes, ignoring the complications introduced by formal consideration of the competitive nature of the reactions. We then consider the reactions as two competitive reactions, determining branching ratios using Troe's vibrational two-channel model. Comparison of the two treatments allows us to assess the utility of the simple model as a quick and dirty tool for assessing branching ratios.

In addition, we consider also the effect upon these results of errors in the quantum chemical calculations. It is commonly accepted that electronic structure methods overestimate barriers to unimolecular reactions. Thus, it is necessary to determine whether the reasonable correction of the quantum chemical barrier heights leads to significantly different relative reaction rates, or branching ratios.

There occurs in the literature several values for the heat of formation of the methoxy radical.[10][31] These values, when combined with the heats of formation of formaldehyde and hydrogen provide the heat of reaction for the dissociation. Using the various experimental values, the heat of reaction may be 22.2 kcal/mole or 26.7 kcal/mole. In a paper on the a priori determination of dissociation energies, we estimated the heat of formation of CH_3O to be 1.0 ± 3.0 kcal/mole.[15] This value has the virtue that the error bars encompass the experimental values; this leads to a dissociation energy estimate equal to 25.1 kcal/mole. Correcting this value for classical translational energy contributions, we obtain the 0K dissociation energy, 24.2 kcal/mole. This sets a lower limit on the critical energy for this reaction channel. The value predicted by the electronic structure calculations for the critical energy corresponds to a recombination barrier of 5.3 kcal/mole, a value several kcal higher than the barrier estimated for the isoelectronic ethyl radical barrier. Thus, there is some evidence that the critical energy for dissociation has been overestimated by several kcal/mole.

Estimating the error for the isomerization reaction barrier is less straightforward. Although we expect that the value exceeds the "true" critical energy, it is difficult to make a reasonable estimate of the error. On the one hand, we believe that the theoretical methods used provide a more reliable prediction of the isomerization barrier than for the dissociation barrier. Conversely, we have not included the contribution of triple excitations on the fourth-order energy contribution; an effect that should reduce the isomerization barrier more than it reduces the dissociation

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31. L. Batt and R.D. McCullough, "Pyrolysis of Dimethyl Peroxide," _Int. J. Chem. Kinetics_, Vol. 8, p. 492, 1976.

barrier. In any case, however, we expect both barriers to be reduced by better theoretical calculations. Therefore, to provide a useful test of the effect of quantum chemical errors on the branching ratios, we assume that the "correct" critical energies are: dissociation 27.0 kcal/mole; isomerization, 30.0 kcal/mole. These values will be used to estimate branching ratios for $T = 1200K$.

In the following sections, we present the results obtained for the rate coefficients by treating the reactions as independent and coupled.

A. Independent Rate Coefficient Treatment

The data used to evaluate the factors in the expression for k_0^{sc} were determined entirely from the results of the quantum chemical calculations which are summarized in Tables 1-3. To estimate a value for the collisions efficiency, we assumed that the average energy transfer in a down collision was 4.6 kj/mole (1.099 kcal/mole), and used Troe's relationship connecting β_c and α. We summarize in Tables 4 and 5 the factors obtained for the dissociation and isomerization reactions, respectively. The values of k_0, given in the right-hand column, lead to the conclusion that the dissociation dominates at room temperature, but that the isomerization reaction competes with dissociation at high temperatures. To some extent the result parallels the change in relative values of the exponential factor, but one should note that the harmonic density of states factor always favors the isomerization reaction. In fact, the density of states factor will always favor the channel with the higher critical energy, since we've evaluated the density of states at E_O. To recapitulate, this model predicts that the isomerization and dissociation reactions compete at high temperature, a result that concurs with Batt's conjecture.

What is the effect on the high-temperature rate coefficients of reducing the critical energies for the two reactions? The detailed results for the two reactions are collected in Table 6. The ratios of the k_0's changes little from that obtained using the original quantum chemical critical energies. Apparently the results of assuming a greater separation between the two critical energies cancel the results of reducing these values. Thus, if we assume that the branching ratio for the competitive reactions can be estimated by computing the rate coefficients independently, we conclude that the isomerization and dissociation reactions compete at high temperature.

B. Vibrational Two-Channel Model

The expression for the total unimolecular rate coefficient, Eq. (8), is very similar to the expression derived by Troe for the low pressure rate coefficient of a single unimolecular reaction. Missing are rotational and anharmonic corrections. The expression, however, contains a term relating to the energy-transfer step size. Since we estimated this value to determine the collision efficiency, β_c, consistency demands retaining the same value in this treatment.

To evaluate the expression[7] for the rate coefficient, k_{20}, requires evaluating the specific branching ratio, $V_2(E)$, given by Eq. (10). The expression for $V_2(E)$, may be rewritten as

TABLE 4. RATE COEFFICIENT CALCULATION DETAILS FOR DISSOCIATION OF CH_3O

T	z_{LJ}	$\rho kT/Q$	F_{anh}	F_E	F_{rot}	$exp(-E_o/kT)$	β_c	k_0
300	2.06(14)	244.0	1.07	1.16	4.06	4.43(-22)	.496	1.6(-6)
600	2.42(14)	363.6	1.07	1.24	2.74	2.11(-11)	.263	1.7(6)
900	2.78(14)	295.7	1.07	1.40	2.13	7.6(-8)	.158	3.0(9)
1200	3.03(14)	192.5	1.07	1.56	1.76	4.6(-6)	.104	8.2(10)

TABLE 5. RATE COEFFICIENT CALCULATION DETAILS FOR ISOMERIZATION OF CH_3O

T	z_{LJ}	$\rho kT/Q$	F_{anh}	F_E	F_{rot}	$exp(-E_o/kT)$	β_c	k_0
300	2.06(14)	356.8	1.07	1.09	3.8	8.02(-24)	.496	1.3(-10)
600	2.42(14)	531.8	1.07	1.22	2.6	3.37(-12)	.263	3.6(5)
900	2.78(14)	433.7	1.07	1.37	2.1	2.25(-8)	.158	1.3(9)
1200	3.03(14)	282.4	1.07	1.53	1.7	1.84(-6)	.104	4.5(10)

TABLE 6. RATE COEFFICIENT DETAILS; MODIFIED CRITICAL ENERGIES, T = 1200K

	z_{LJ}	$\rho kT/Q$	F_{anh}	F_E	F_{rot}	$exp(-E_o/kT)$	k_0^{sc}
Dissociation	3.03(14)	121.9	1.07	1.6	1.70	1.3(-5)	1.39(12)
Isomerization	3.03(14)	209.8	1.07	1.56	1.70	3.7(-6)	6.6(11)

$$V_2(E) = \frac{W_2(E)}{W_1(E)+W_2(E)} \quad , \tag{11}$$

where $W_1(E)$ indicates the number of open vibrational reaction channels for the products of the lower critical energy pathway. Thus, one can determine $V_2(E)$ by counting the number of open channels at each energy for each pathway. Since the critical energies for the two reaction paths are so nearly equal, the specific branching ratio should vary only slightly with energy near E_{02}, so we follow Troe and assume that

$$V_2(E) \simeq V_2(E_{02}) \quad .$$

Finally, rather than count the number of reactant channels open for each pathway, we assume that the specific branching ratio can be approximated substituting the vibrational partition functions for the two activated complexes. This approximation has no formal justification, but since we have estimates of the vibrational eigenvalues orthogonal to the reaction coordinate, we assume that the populations of these states provides an approximation to the number of available channels for each pathway. This leaves us to evaluate the trivial integral,

$$\int_{E_{02}}^{\infty} \exp\left(-\frac{(E_o-E_{02})(\alpha+F_E kT)}{\alpha F_E kT}\right) \quad , \tag{12}$$

Evaluating the expressions, using the data from Table 5, we find that for $T = 300$

$$k_{20} \simeq .002 \; k_0 \quad ,$$

while for $T = 1200K$

$$k_{20} \simeq .023 \; k_0$$

Since

$$k_{10} = k_0 - k_{20} \quad ,$$

it is obvious that the two-channel model does not predict the isomerization reaction to compete with the dissociation reaction, even at $T = 1200K$. This result depends, however, upon the estimates of the energy transfer parameter, α, the dilemma faced when trying to use unimolecular models as predictive models.

The electronic structure calculations summarized in this report provide information about the potential energy hypersurface for the methoxy radical reactions that has not been available heretofore. To some extent, Troe's desire for details of the potential energy surface has been satisfied. Nonetheless, two simplified models for rate coefficient estimates provide qualitatively different descriptions of the relative importance of the two reaction channels. This result demonstrates the need for more precise descriptions of the energy transfer processes that dominate the low-pressure unimolecular reactions.

V. CONCLUSIONS

The results of this study do not provide a definitive demonstration that the isomerization reaction of the methoxy radical competes with the dissociation reaction. One simplified dynamical model suggests that the reactions do compete at high temperature. However, Troe's model for two-channel thermal unimolecular reactions predicts that the isomerization reaction does not compete with the dissociation reaction. The latter result, however, depends strongly upon the details of the energy-transfer processes that control the low-pressure rates, and on the rather gross approximations we've used in applying that model.

Variation of the predicted critical energies to values that intuition suggests are closer to reality, leads to virtually no change in the branching ratio predicted by the uncoupled dynamical model. The rate coefficient estimates, however, do change significantly, indicating that predictive rate coefficient models yet await more accurate quantum chemical calculations.

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